

Adsorption of Ammonia on Regenerable Carbon Sorbents

Marek A. Wójtowicz¹, Joseph E. Cosgrove², and Michael A. Serio³
Advanced Fuel Research, Inc., East Hartford, CT, 06108

and

Monique Wilburn⁴
NASA Johnson Space Center, Houston, TX 77058

Results are presented on the development of reversible sorbents for the combined carbon dioxide, moisture, and trace-contaminant (TC) removal for use in Extravehicular Activities (EVAs), and more specifically in the Primary Life Support System (PLSS). The currently available life support systems use separate units for carbon dioxide, trace contaminants, and moisture control, and the long-term objective is to replace the above three modules with a single one. Data on sorption and desorption of ammonia, which is a major TC of concern, are presented in this paper. The current TC-control technology involves the use of a packed bed of acid-impregnated granular charcoal, which is non-regenerable, and the carbon-based sorbent under development in this project can be regenerated by exposure to vacuum at room temperature. In this study, several carbon sorbents were fabricated and tested for ammonia sorption. Ammonia-sorption capacity was related to carbon pore structure characteristics, and the temperature of oxidative carbon-surface treatment was optimized for enhanced ammonia-sorption performance.

Nomenclature

<i>AFR</i>	=	Advanced Fuel Research, Inc.
<i>BDDT</i>	=	Brunauer, Deming, Deming, and Teller
<i>BET</i>	=	Brunauer, Emmett, and Teller
<i>CMS</i>	=	Carbon Molecular Sieve
<i>DFT</i>	=	Density Functional Theory
<i>D-A</i>	=	Dubinin-Astakhov
<i>D-R</i>	=	Dubinin-Radushkevich
<i>EVA</i>	=	Extravehicular Activity
<i>FTIR</i>	=	Fourier Transform Infrared
<i>MGA</i>	=	Multi-Gas Analyzer
<i>MFC</i>	=	mass-flow controller
<i>NA</i>	=	not available
<i>NASA</i>	=	National Aeronautics and Space Administration
<i>PLSS</i>	=	Primary Life Support System
<i>ppi</i>	=	pores per inch
<i>PVDC</i>	=	polyvinylidene chloride
<i>RVC</i>	=	reticulated vitreous carbon
<i>TC</i>	=	Trace Contaminant
<i>TCCS</i>	=	Trace Contaminant Control System
<i>V</i>	=	pore volume, cm ³ /g

¹ Vice President, Clean Energy & Carbon Materials, Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108.

² Senior Engineer, Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108.

³ President, Advanced Fuel Research, Inc., 87 Church Street, East Hartford, CT 06108.

⁴ PLSS Engineer, NASA Johnson Space Center, EC5 - Space Suit & Crew Survival Systems, Houston, TX 77058.

w	=	pore width, nm
ΔV_2	=	pore volume in the pore-width range 0.9–2.2 nm, cm^3/g
ΔV_3	=	pore volume in the pore-width range 2.2–5.0 nm, cm^3/g

I. Introduction

THE NASA objective of expanding the human experience into outer space requires the development of regenerable life support systems. This study addresses the development of regenerable carbon sorbents for trace-contaminant (TC) removal for the space suit used in Extravehicular Activities (EVAs); this paper does not address the design of an actual air-revitalization system. Currently, a bed of granular activated carbon is used for TC control, the main trace contaminant of interest being ammonia. The carbon is impregnated with phosphoric acid to enhance ammonia sorption, but this also makes regeneration difficult, if not impossible. Temperatures as high as 200 °C have been shown to be required for only partial desorption of ammonia on time scales of 18–140 hours¹, which makes regeneration impractical. Thus, the activated carbon has been treated as an expendable resource and the sorbent bed has been oversized in order to last throughout the entire mission [23 kg carbon for cabin-air revitalization and about 1 lb (0.454 kg) for the space suit]. Another important consideration is pressure drop. Granular sorbent offers significant resistance to gas flow, which is associated with a high demand for fan power. Thus, there is a great need for an effective TC sorbent that could be regenerated by short exposure to vacuum at low temperatures (under 80 °C for less than 1 hour). A monolithic structure (e.g., a honeycomb), or a sorbent in the form of open-porosity foam, is also desired to reduce pressure drop, and consequently fan-power consumption.

The current state of the art and historical approaches to trace-contaminant removal in the primary life support system (PLSS), often referred to as the space suit backpack, were reviewed by Paul and Jennings¹. Activated carbon (charcoal) was identified as a preferred sorbent for the trace contaminant control system (TCCS) application in terms of effectiveness, simplicity, and maturity of this technological solution. Carbon regeneration, however, has always been problematic, mainly because all carbons used to date were impregnated with phosphoric acid or other acidic compounds. This results in a virtually irreversible chemical reaction with ammonia and salt formation, which greatly complicates regeneration. Even though some TCs can be removed from acid-impregnated carbons, this is typically associated with a tremendous reduction in adsorption capacity after regeneration. It has been widely believed that unimpregnated carbon does not adsorb ammonia (see, for example, Ref. 2–4), and that chemisorption is the only option to bind ammonia to the carbon surface. We believe this is true only for carbons with a fairly wide distribution of pore sizes, i.e. for almost all commercial carbons. If the pore size could be optimized, however, in such a way so that almost all pores have the right size for ammonia physisorption, it is our belief that no chemical impregnation would be necessary to effect ammonia sorption. Furthermore, physisorbed ammonia should be easier to desorb using vacuum regeneration as no chemical bonds would have to be broken. To ensure high ammonia-sorption capacity of a carbon adsorbent, the predominant pore sizes should be in the range close to molecular dimensions of the adsorptive (ammonia) so that the van der Waals interactions are strong. This argument narrows down the choice of preferred sorbents to carbon molecular sieves (CMS), such as carbons derived from polyvinylidene chloride (PVDC) or polyfurfuryl alcohol. A unique feature of CMS materials is a narrow pore-size distribution, with almost all pores residing in the micropore region (pores smaller than 2 nm)⁵. We are unaware of any systematic studies that address the effect of carbon pore structure on ammonia sorption and the regeneration performance of trace-contaminant sorbents.

We believe that a non-optimal sorbent structure, both internal (broad pore-size distribution) and external (intraparticle heat transfer limitations), combined with chemical impregnation, has led to extremely long sorbent regeneration time scales on the order of 5–140 hours depending on temperature (130–200 °C)¹. In this study, we examine the use of PVDC-derived granular carbon and carbon-foam structures for reversible ammonia sorption/desorption as a function of pore structure and carbon pre-treatment. The main focus of the project is vacuum regeneration, but rapid resistive heating to moderately low temperatures (up to 80 °C) should also be considered as an optional feature that could accelerate the vacuum regeneration process. Such regeneration could be performed, for example, on board spacecraft after an extravehicular activity (EVA) has been completed. The time scale associated with a single EVA is not expected to exceed eight hours, which defines sorbent-performance requirements.

We believe that good TC-sorption capacity can be accomplished through the combination of a particularly favorable pore structure for optimum physical adsorption (physisorption) of TCs and carbon-surface conditioning that enhances adsorption without adversely affecting vacuum regeneration. Such enhancement of ammonia-sorption capacity by thermal oxidation of the carbon surface was reported previously^{6,7}. The avoidance of acid impregnation of carbon further helps the cause of adsorption reversibility. Finally, the issue of pressure drop and fan-power

requirement is addressed through the use of a thin carbon sorbent layer deposited on vitreous carbon foam structure with fairly open porosity (30–80 pores per inch, ppi).

The objectives of this work are: (1) to examine the relationship between ammonia-sorption capacity and carbon pore-structure characteristics; and (2) to optimize the temperature at which carbon-surface conditioning is implemented.

The innovations explored in the approach advocated in this study are: (1) vacuum (or vacuum/thermal) regenerable operation, in contrast to the currently used bed of expendable sorbent; (2) TC removal based on *reversible physisorption* on high-purity carbon rather than on *irreversible chemisorption* on activated carbon impregnated with acidic compounds; (3) a carbon monolith/foam sorbent, in contrast to the currently used bed of granular charcoal; (4) carbon surface conditioning (oxidation) to enhance TC sorption without adversely affecting sorbent regeneration; (5) low pressure drop; (6) carbon pore structure tailored for optimal vacuum/thermal regeneration; (7) the possibility of resistive heating of the carbon monolith/foam for rapid regeneration; and (8) good resistance to dusty environments.

II. Materials and Experimental Techniques

A. Granular Carbon

More than 30 samples of granular PVDC carbon were tested for ammonia sorption using the experimental set-up described in section II.E. Eight granular sorbents (A through H) were obtained from a collaborator, and other carbon sorbents were prepared in-house. All sorbents used in this study were obtained by carbonization of PVDC. The samples prepared in-house were produced from two different PVDC precursors, each of them procured from a different source: Allied Signal, currently Honeywell, and Goodfellow. All granular carbon samples were ground and sieved to the +45/-20 mesh size (mean particle diameter ≈ 0.549 mm) prior to ammonia-sorption analysis.

B. Carbon Sorbent Supported on Vitreous Carbon Foam

A number of carbon sorbents supported on vitreous carbon foam were prepared using the dry powder coating technique described in references [6,7]. The support structure employed in this work was Duocel[®] foam manufactured by ERG Aerospace Corporation. This foam is described as an open-cell, porous structure consisting of an interconnected network of solid “struts,” the porosity of which is determined by the number of pores per inch (ppi). 80 ppi foam was used in this work.

C. Carbon-Surface Treatment by Oxidation in Air

As described below, and also in references [6,7], surface conditioning of the PVDC carbon via thermal oxidation at modest temperatures had a dramatic effect on ammonia adsorption. For experiments performed in this study, PVDC-carbon samples were oxidized in ambient air at temperatures ranging from 200 °C to 400 °C for 24 hours. At 200 °C, none of the samples showed any measurable weight loss after oxidation. At higher temperatures, however, some weight loss was observed due to carbon gasification.

D. Carbon Characterization

A fully automated gas-sorption system Quantachrome ASiQwin was used for collecting and processing nitrogen-isotherm data for carbon sorbents prepared in-house. Pore-structure characterization for other sorbents was provided by the supplier. Prior to adsorption-isotherm measurements, each sample was outgassed under vacuum at 300 °C for at least 3 hours. Nitrogen-adsorption isotherms were then determined at 77 K, and these data were used to perform the following analyses: (a) BET surface area; (b) pore volume; (c) Dubinin-Radushkevich (D-R) micropore surface area and micropore volume; and (d) pore-size distribution of micropores using the Density Functional Theory (DFT).

E. Experimental Set-up and Procedures for Sorbent Testing

Figure 1 shows a schematic of the testing system used in this study. The system makes it possible to measure the adsorption capacity of carbon sorbents in the presence of all gases of interest: carbon dioxide (CO₂), ammonia (NH₃), formaldehyde (CH₂O), oxygen (O₂), nitrogen (N₂), and water vapor (H₂O), although only NH₃, CO₂, O₂, and N₂ were present in the tests performed in this part of the project. The apparatus incorporates a Fourier transform infrared (FTIR) spectrometer-based On-Line Technologies model 2010 Multi-Gas Analyzer (MGA) for quantification of infrared-active gas species, including ammonia. Using mass-flow controllers, the initial gas

mixtures are blended to achieve the desired gas concentration, which are: ~20 ppm ammonia, ~1.0 vol% carbon dioxide, 29.3 vol% oxygen, and balance nitrogen. For humidifying the gas stream, the nitrogen stream is re-routed through a water bubbler, but the measurements reported here were performed using dry gas. It was shown in a previous study⁶ that the presence of moisture in the gas stream enhanced ammonia sorption by PVDC carbon sorbents. During sorbent testing, the final mixture is first directed through a sample bypass line, to establish the baseline gas concentration and flow rate. It is then re-directed through the sample “cell” for sorbent adsorption testing. The sample cell consists of a quartz or glass tube that contains the sorbent. It is mounted in a vertical orientation, with the gas inlet at the top of the cell so that gas flow is in a downward direction. For tests involving granular sorbents, a 5.6 mm inner diameter tube is used, whereas a tube having an inner diameter of 22 mm is used for testing sorbents supported on vitreous foam. In either case, the carbon sample is supported inside the tube with ceramic wool on both ends. The typical bed heights for the small and large diameter tubes are 10 mm and 12.5 mm, respectively. At a gas flow rate of 1.2 L/min, the above tube bed geometries correspond to a gas residence time within the bed of 0.012 s and 0.238 s for the small and large beds, respectively.

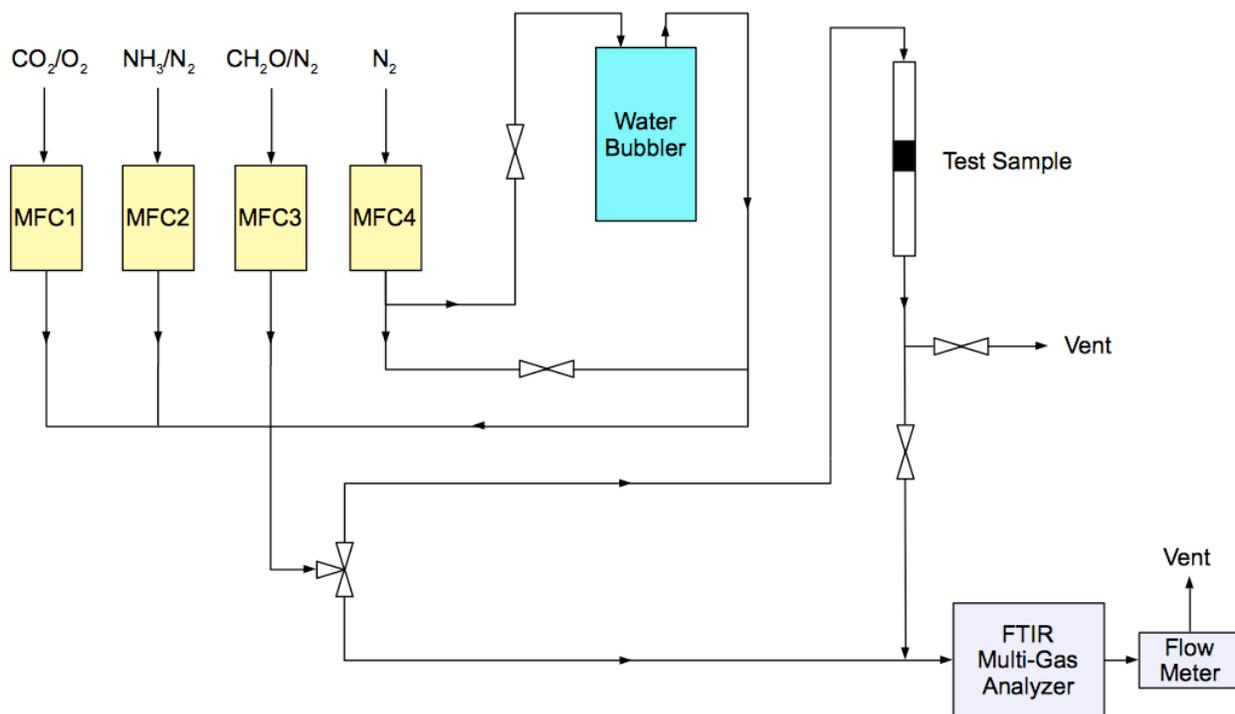


Figure 1. A schematic representation of the sorption testing apparatus; *MFC1*, *MFC2*, *MFC3*, and *MFC4* are mass-flow controllers.

For experiments involving sorbent regeneration in vacuum, the sample cell was removed from the test stand and installed in a high-vacuum chamber pumped by a turbomolecular pump (base vacuum of $\sim 10^{-6}$ Torr). After the vacuum regeneration, the sample cell was re-installed on the test stand and the ammonia adsorption was measured again to determine the regenerated capacity.

III. Results and Discussion

A. Carbon Characterization

PVDC carbon is known to be extremely microporous, i.e. having most of its porosity associated with pore widths smaller than 2 nm; the BET surface area of such carbon is usually close to $1000 \text{ m}^2/\text{g}$ ^{5,8,9}. Nitrogen-adsorption isotherms determined in this study were found to be of Type I according to the classification of Brunauer, Deming, Deming, and Teller (BDDT)¹⁰, which is indeed characteristic of microporous materials⁵. An example of such an isotherm is shown in Figure 2 for carbon *E*, and changes in the isotherm shape caused by carbon-surface oxidation at temperatures in the range 200–350 °C can also be seen in Figure 2. The slope of the initially flat isotherm becomes

more pronounced for oxidized samples. Since some weight loss upon oxidation was observed, as shown in Table 1, it is fair to conclude that the changes in the isotherm shape are due to carbon gasification in air. Pore-structure characteristics derived from adsorption isotherms, such as BET surface area, D-R micropore volume, and D-R adsorption energy are presented in Table 1. Referring to Figure 2, it is interesting to note that although the amount of nitrogen adsorbed on carbon *E* initially increases with oxidation temperature, i.e. with the degree of gasification, or surface activation, the most severely oxidized carbon exhibits weaker nitrogen adsorption. This is most likely due to pore enlargement and the associated weakening of the van der Waals interactions within the pore structure. This interpretation is supported by the decrease in the D-R adsorption energy, which reflects the weakening of ammonia-carbon interactions in larger pores.

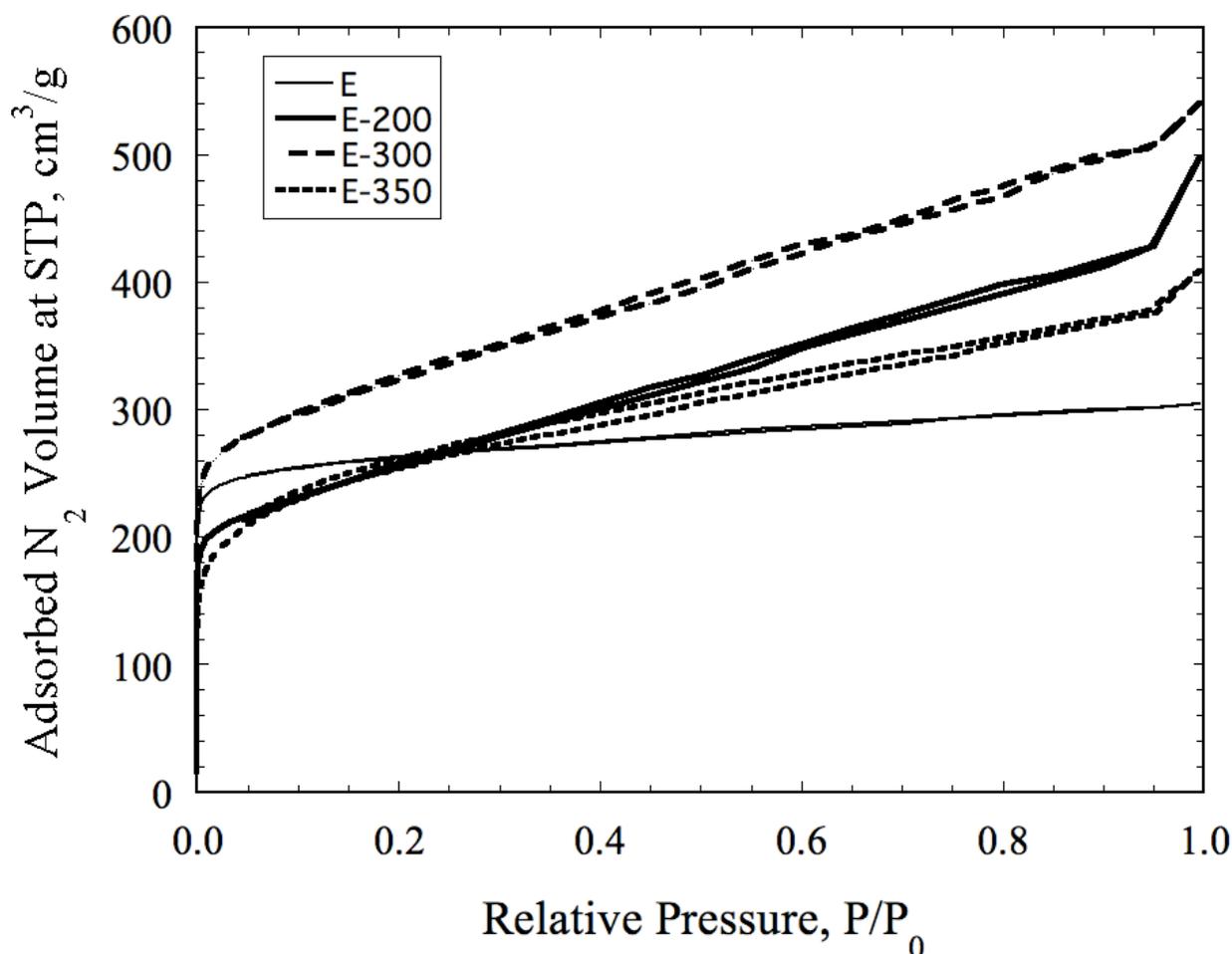


Figure 2. Nitrogen-adsorption isotherms determined at 77 K for carbon *E*, and for carbon *E* oxidized in air for 24 hours at different temperatures. The number following a hyphen in carbon designation indicates oxidation temperature in degrees Celsius.

The BET surface area of PVDC carbons was found to be generally in the range of 909–1811 m²/g, which is in agreement with literature data⁵. Carbon *H*, which has a nitrogen BET surface area of 721 m²/g, is an exception, presumably due to the small micropores that proved to be too difficult to access for nitrogen at 77 K. In any case, the BET surface area is not believed to be a meaningful characteristic of microporous materials. Gregg and Sing point out that "the very concept of the surface area of a microporous solid is of doubtful validity, and that whilst it is possible to obtain an estimate of the total micropore *volume* from a Type I isotherm, only the crudest guesses can be made as to the pore size *distribution*¹¹."

Table 1. A list of granular-carbon/carbon-foam sorbents used in this study and their ammonia-sorption capacities. *BET S.A.* is BET surface area, *D-R* refers to the Dubinin-Radushkevich analysis, ΔV_2 and ΔV_3 are volumes of pores in pore-size ranges 0.9–2.2 nm and 2.2–5.0 nm, respectively. The number following a hyphen in sample *ID* refers to the temperature of carbon-surface oxidation (°C), and *R* followed by a numeral in sample *ID* indicates sorbent regeneration time (hours) prior to ammonia-sorption measurement. Carbon-characterization data have been derived from nitrogen-adsorption isotherms at 77 K, and ΔV_1 and ΔV_2 data are based on the Density Functional Theory (DFT) analysis. All ammonia-sorption capacities are related to PVDC-carbon weight, excluding the weight of vitreous foam, if used.

Sample ID	Precursor (Geometry)	BET S.A. (m ² /g)	D-R Micropore Volume (cm ³ /g)	ΔV_2 (cm ³ /g)	ΔV_3 (cm ³ /g)	D-R Adsorption Energy (kJ/mol)	Loss on Oxidation (wt%)	Adsorption Capacity (mg NH ₃ /g)
A	NA (granular)	1016	0.413			29.1		0.3
A-300	NA (granular)						6.4	4.1
B	NA (granular)	933	0.375			31.3		0.25
B-300	NA (granular)						3.4	3.3
C	NA (granular)	979	0.394			30.2		0.16
C-300	NA (granular)						3.1	3.3
D	NA (granular)	1811	0.752			21.2		0.22
D-300	NA (granular)						4	1.1
E	NA (granular)	1031	0.394	0.061	0.047	30.4		0.3
E-200	NA (granular)	909	0.336	0.049	0.232	29.0	0	0.53
E-300	NA (granular)	1167	0.433	0.084	0.236	28.2	6.3	5.8
E-350	NA (granular)	922	0.321	0.168	0.159	21.7	34.8	19.3
E-400	NA (granular)						83	11.8
F	NA (granular)	1024	0.414			28.8		0.2
F-300	NA (granular)						2	1.9
G	NA (granular)	1148	0.426	0.045	0.268	31.5		1.1
G-200	NA (granular)						0	2.74
G-300	NA (granular)	1397	0.516	0.203	0.250	22.6	32.3	14.8
G-300-R6	NA (granular)						32.3	4.8
H	NA (granular)	721	0.294			28.9		0.047
H-200	NA (granular)						0	0.058
012815	Honeywell (granular)	1124	0.425	0.047	0.180	32.4		0.42
012815-300	Honeywell (granular)	1400	0.508	0.173	0.218	25.3	13.3	13.2
012815-300-R6	Honeywell (granular)						13.3	5
020415	Honeywell (granular)							0.64
020415-300	Honeywell (granular)						18.6	15.5
021115A-300	Honeywell (foam)						14	19.7
	Honeywell (foam)							11.1
021115B	Honeywell (foam)							0.36
021115B-350	Honeywell (foam)						52.7	34.6
021115B-350-R6	Honeywell (foam)						52.7	16.4
021115B-350-R12	Honeywell (foam)						52.7	18.5
021115B-350-R1.5	Honeywell (foam)						52.7	14.1
021115B-350-R0.25	Honeywell (foam)						52.7	7.6
021115C	Honeywell (foam)							
021115D-300	Goodfellow (foam)						0	8.8
021115E	Goodfellow (foam)							0.26
021115E-350	Goodfellow (foam)						27.4	20.4
021115E-350-R6	Goodfellow (foam)							11
Ammonasorb	NA (granular)							23.7
Ammonasorb-R6	NA (granular)							6.88

*For samples A, B, C, D, E, F, G, and H, the Dubinin-Astakhov (D-A) analysis was used instead of the Dubinin-Radushkevich (D-R) analysis, and the mean value of the exponent was 1.78 ± 0.06 (at a 95% confidence level).

In spite of the difficulties noted above, pore-size distributions obtained using the Density Functional Theory were found to reveal a consistent pattern for the PVDC carbons used in this work. A typical DFT pore-size distribution is shown in Figure 3, where three distinct pore-size regions can be identified: (1) pores smaller than 0.9 nm, where quantification is difficult due to experimental limitations associated with characterizing pores with sizes close to molecular dimensions at low values of P/P_0 ; (2) pores with sizes in the range of 0.9–2.2 nm, where two

distinct or somewhat overlapping peaks are observed; and (3) pores with sizes in the range of small mesopores: 2.2–5.0 nm. Pore volumes associated with pore-size regions (2) and (3) are denoted ΔV_2 and ΔV_3 , respectively, and they are included in Table 1 together with other pore-structure characteristics.

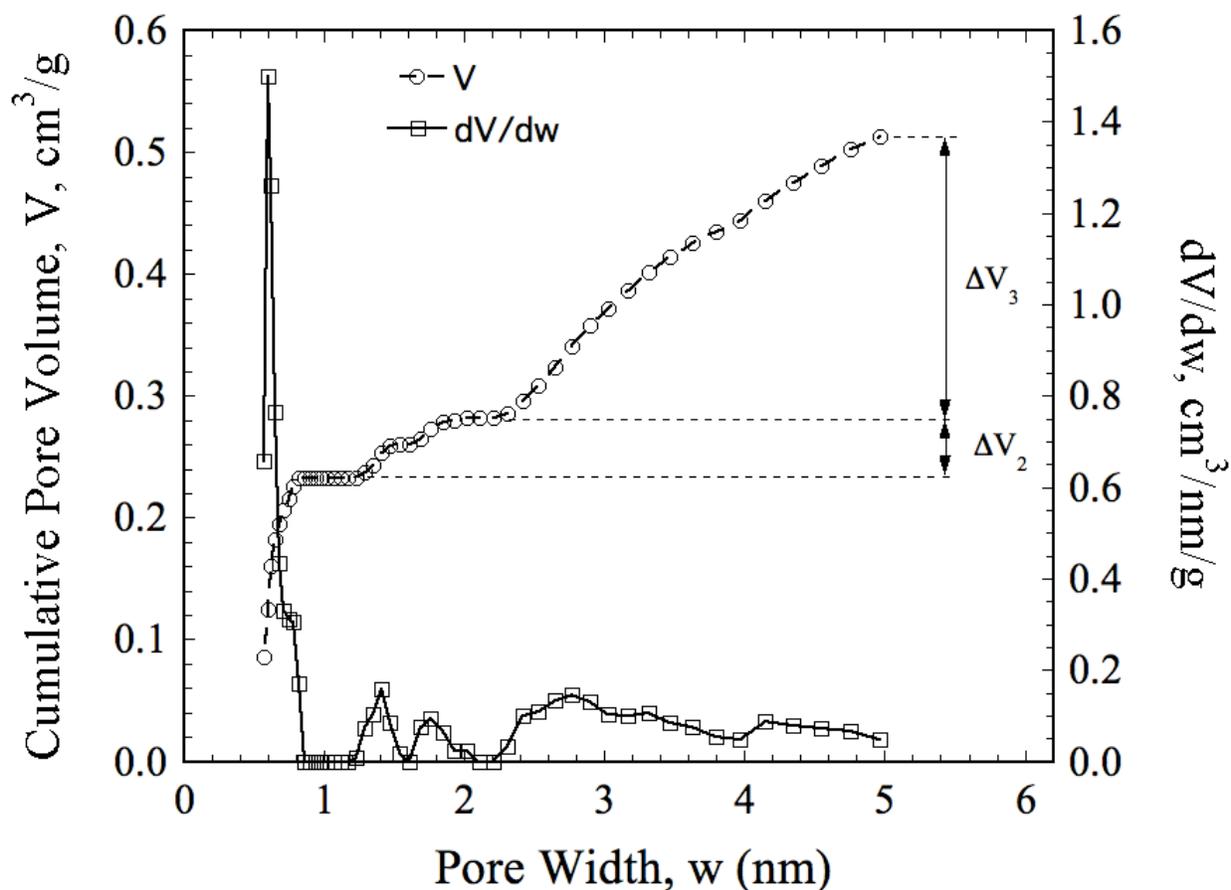


Figure 3. The DFT pore-size distribution for carbon E-200.

B. Ammonia Sorption and Sorbent Regeneration

A number of PVDC-carbon sorbents were tested for ammonia adsorption and desorption. Table 1 summarizes details related to sample identity and preparation conditions, e.g., surface oxidation temperature. The table also provides ammonia-sorption capacity measured for each sample. In addition to PVDC-carbon samples, Table 1 includes results for Ammonasorb II, the activated carbon impregnated with phosphoric acid, which is currently used for TC control by NASA. Several carbon sorbents were subjected to adsorption-regeneration cycles, and ammonia-sorption capacities after sorbent vacuum regeneration are also reported in Table 1.

In general, ammonia-sorption data can be presented in terms of either breakthrough curves, which are plots of ammonia concentration at the adsorber outlet as a function of time, or as sorption-capacity curves, which are integrals of breakthrough curves. Although the information included in both types of curves is equivalent, most literature ammonia-sorption data have been reported in terms of sorption-capacity curves (e.g., see Ref. 3, 4, and 6), and the same convention is followed in this paper.

The Effect of Surface Oxidation and Vacuum Regeneration—A few typical ammonia sorption capacity curves are shown in Figure 4, and they illustrate the tremendous enhancement of ammonia sorption caused by the oxidative carbon-surface treatment by exposure to air. This effect was the subject of a previous publication⁶, as well as the question of ammonia sorption reversibility, i.e. sorbent regeneration by exposure to vacuum. The data obtained in this study show the improved PVDC-sorbent performance to the point of matching, and in one case even greatly exceeding, the sorption capacity of Ammonasorb, as shown in Table 1. Furthermore, the loss of sorption capacity

following the first regeneration cycle is smaller in the case of PVDC carbons (~53%) as compared with the 71% loss of sorption capacity for Ammonasorb.

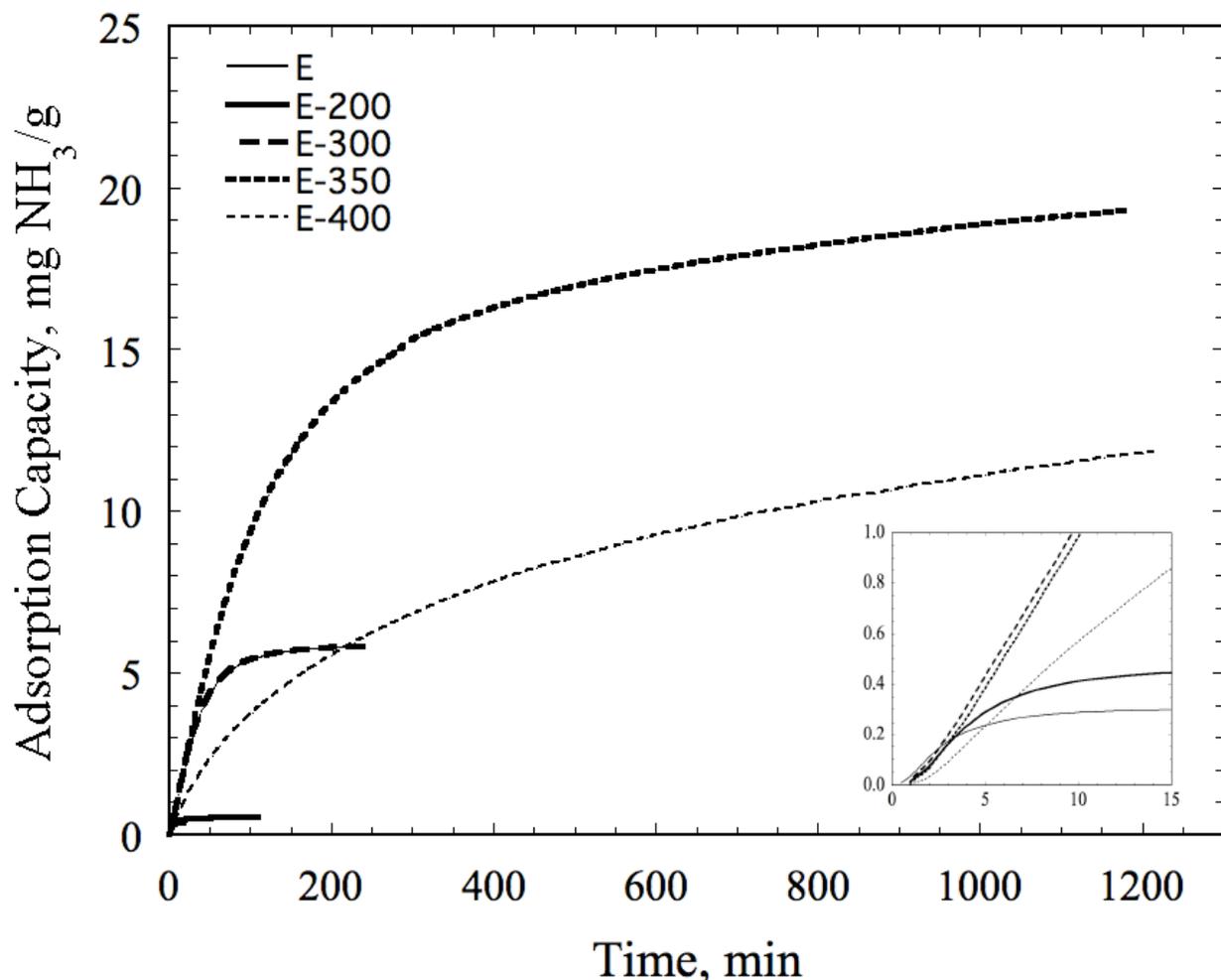


Figure 4. Ammonia sorption capacity curves for sorbent *E* prior and after surface oxidation by exposure to air at temperatures indicated (in degrees Celsius) after the hyphen in sample designation in the legend. The inset shows sorption-capacity curves at early stages of ammonia sorption.

The Relationship Between Ammonia-Sorption Capacity and Pore-Structure Characteristics – This relationship is difficult to capture and quantitatively describe in view of the challenges associated with the meaningful characterization of microporous carbons, as discussed in section III.A. An attempt to relate sorption capacity to pore structure of carbon *E* is shown in Figure 5. It can be seen that ammonia-sorption capacity does not correlate very well with any of the parameters derived from nitrogen adsorption isotherm data, except for ΔV_2 , the volume of pores in the range 0.9–2.2 nm.

In view of the above result, it is hypothesized that pores with dimensions between 0.9 nm and 2.2 nm are large enough to provide easy access for ammonia molecules into the microporous structure of sorbent, at the same time being sufficiently small to ensure that the strong van der Waals forces facilitate large adsorption capacity. The kinetic diameter of ammonia molecules can be calculated using the Stockmayer potential. This molecular size was reported to be 0.26 nm in one literature reference¹², and 0.326 nm in another¹³. In either case, the molecular dimensions seem consistent with good adsorption capacity in pores having the width of 0.9–2.2 nm.

If further experiments confirm the above correlation between ammonia-sorption capacity and pore volume in the pore-size range of 0.9–2.2 nm, the DFT calculations may prove quite useful in predicting sorbent performance on the basis of standard nitrogen adsorption isotherm data.

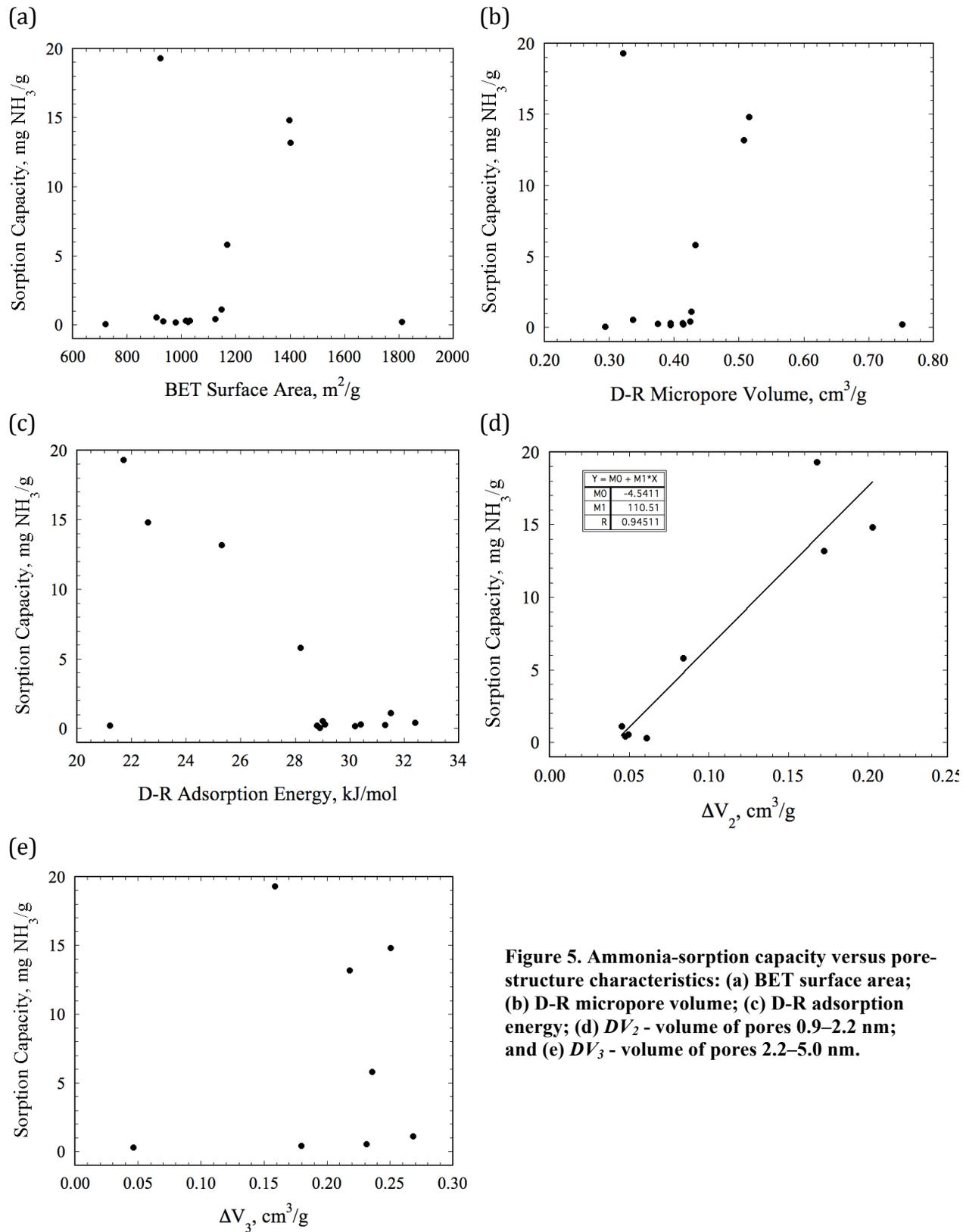


Figure 5. Ammonia-sorption capacity versus pore-structure characteristics: (a) BET surface area; (b) D-R micropore volume; (c) D-R adsorption energy; (d) DV_2 - volume of pores 0.9–2.2 nm; and (e) DV_3 - volume of pores 2.2–5.0 nm.

Oxidation Temperature Optimization - Data shown in Figure 6 indicate that the optimum oxidation temperature for sample *E* is close to 350 °C as ammonia-sorption capacity drops at 400 °C, and this is also associated with an 83% carbon loss due to gasification (see Table 1).

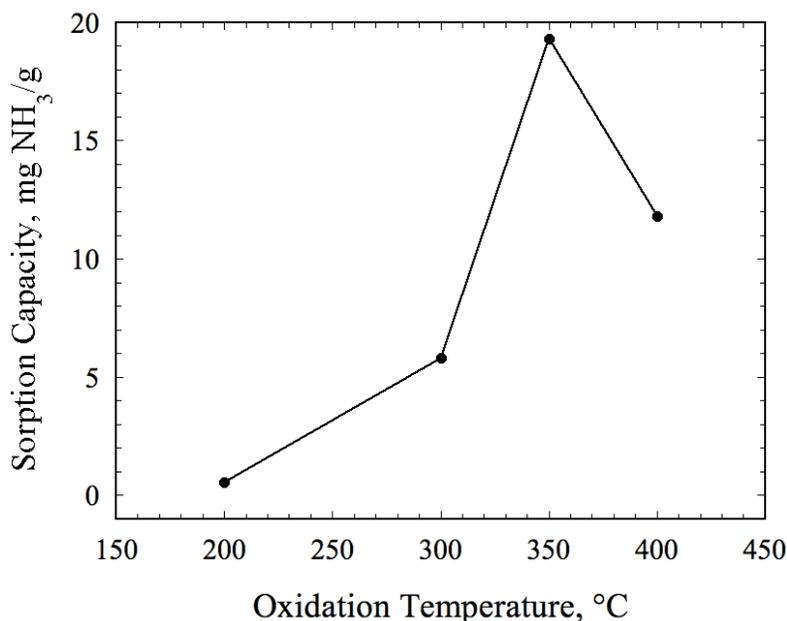


Figure 6. Ammonia-sorption capacity versus oxidative surface treatment temperature for sorbent *E*.

IV. Conclusions

More than 30 PVDC-carbon sorbents were fabricated and tested for ammonia sorption in a fixed-bed adsorber. Effective carbon surface conditioning via oxidation was found to strongly enhance ammonia sorption without impairing sorbent regeneration, which confirmed results from a previous study⁶. Ammonia-adsorption capacity of PVDC-based sorbents was found to match, and in one case even exceed, the sorption capacity of Ammonasorb II, a phosphoric-acid impregnated activated carbon. Ammonia sorption was related to pore-structure characteristics derived from nitrogen adsorption isotherm data, and it was found to correlate with the volume of pores having sizes in the range 0.9–2.2 nm. The temperature of carbon oxidative treatment was varied between 200 °C and 400 °C, and the optimum was found close to 350 °C.

Acknowledgments

Financial support for the project was provided by the National Aeronautics and Space Administration (NASA) under Contract No. NNX14CJ09C. Nitrogen-adsorption measurements for carbon samples prepared in-house were performed by Dr. Indrek Külaots of Brown University. The above contributions are gratefully acknowledged.

References

¹Paul, H. L. and Jennings, M. A., "Results of the trace contaminant control trade study for space suit life support development," Proc. 39th Int. Conf. on Environmental Systems (ICES), Savannah, Georgia, July 12-16, 2009, SAE technical paper No. 2009-01-2370, SAE International, 2009.

²http://en.wikipedia.org/wiki/Activated_carbon

³Luna, B., Podolske, J., Ehresmann, D., Howard, J., Salas, L. J., Mulloth, L., and Perry, J. L., "Evaluation of commercial off-the-shelf ammonia sorbents and carbon monoxide oxidation catalysts," Proc. 38th Int. Conf. on Environmental Systems (ICES), San Francisco, California, June 29-July 2, 2008, SAE technical paper No. 2008-01-2097, SAE International, 2008.

⁴Luna, B., Somi, G., Winchester, J. P., Grose, J., Mulloth, L., and Perry, J., "Evaluation of commercial off-the-shelf sorbents and catalysts for control of ammonia and carbon monoxide," Proc. 40th Int. Conf. on Environmental Systems (ICES), Barcelona, Spain, July 11-15, 2010, AIAA technical paper No. 2010-6062, AIAA, 2010.

⁵Walker, P. L., Jr., Austin, L. G., and Nandi, S. P., "Activated Diffusion of Gases in Molecular-Sieve Materials," in *Chemistry and Physics of Carbon*, P. L. Walker, Jr. (Ed.), vol 2, Marcel Dekker, New York, 1966.

⁶Wójtowicz, M. A., Cosgrove, J. E., Serio, M. A., and Jennings, M. A., "Reversible ammonia sorption on carbon for the Primary Life Support System (PLSS)," *Proc. 42nd Int. Conf. on Environmental Systems (ICES)*, San Diego, California, July 15-19, technical paper No. AIAA-2012-3437, AIAA, 2012.

⁷Wójtowicz, M. A., Cosgrove, J. E., and Serio, M. A., "Carbon sorbent for reversible ammonia sorption," U.S. Patent pending (all claims accepted; to be issued in 2015).

⁸Wójtowicz, M. A., Markowitz, B. L., Smith, W. W. and Serio, M. A., "Microporous carbon adsorbents for hydrogen storage," *Int. Journal of the Society of Materials Engineering for Resources* 7 (2), 253–266, 1999.

⁹Wójtowicz, M. A., Florczak, E., Kroo, E., Rubenstein, E., Serio, M. A., and Filburn, T., *Carbon-Supported Amine Monoliths for Carbon Dioxide Removal*, Final Report, NASA Phase I SBIR contract No. NAS9-03012, Advanced Fuel Research, East Hartford, CT, July 2003.

¹⁰Brunauer, S., Deming, L. S., Deming, W. S., and Teller, E., *J. Amer. Chem. Soc.* **62**, 1723, 1940.

¹¹Gregg, S. J. and Sing, K. S., *Adsorption, Surface Area and Porosity*, 2nd ed., Academic Press, Harcourt Brace & Company, London, 1982, Chap. 1, p. 37.

¹²Breck, D. W., *Zeolite Molecular Sieves: Structure, Chemistry and Use*, Wiley, New York, 1974, 593–724.

¹³van Leeuwen, M. E., "Derivation of Stockmayer potential parameters for polar fluids," *Fluid Phase Equilib.* **99**, 1–18, 1994.